

X-Ray Analysis of the Crystal Structure of Durene.

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1. *Crystal Data, Space Group.*

The crystal structure of durene, 1.2.4.5. (sym.)-tetramethyl benzene, $C_6H_2(CH_3)_4$, has not previously been examined by the X-ray method, but the class and axial ratios are given by Groth* as monoclinic prismatic

$$a : b : c = 2.4609 : 1 : 1.9975, \quad \beta = 115^\circ 27'$$

with the (100) face most prominently developed. The present work confirms these measurements to within the limits of experimental error (about $\frac{1}{2}\%$), but it is found that the axial directions used above define a cell which contains an identical molecule at the centre of the ac face. It is therefore necessary to select a new axis in order to define the true unit cell. The relation of Groth's axial directions to the cell now chosen is illustrated in fig. 1, the b axis being perpendicular to the paper.

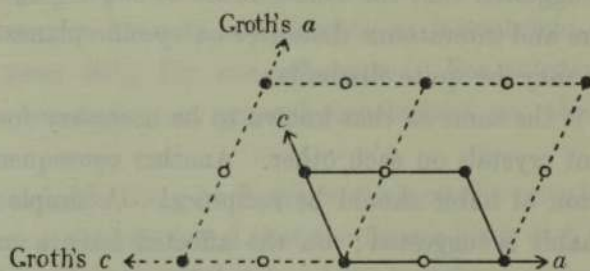


FIG. 1.—Unit cell of durene.

The X-ray work, recorded by means of rotation, oscillation, and moving film photographs, leads to the following values for the axial lengths, etc. :—

$$a = 11.57 \pm 0.05 \text{ \AA.}$$

$$b = 5.77 \pm 0.02 \text{ \AA.}$$

$$c = 7.03 \pm 0.05 \text{ \AA.}$$

$$\beta = 113.3^\circ \quad \{h01\} \text{ halved when } h \text{ is odd, } (010) \text{ halved.}$$

Space group $C_{2h}^5 (P2_1/a)$

Density of crystal = 1.03 (Iball)

Number of molecules of $C_{10}H_{14}$ per unit cell = 2 (1.99)

Volume of unit cell = 430 \AA.^3 .

* 'Chem. Krystallog.', vol. 4, p. 758 (1917).

Reference to space group literature will show that under these circumstances a centre of symmetry must be assigned to the molecule, and that this is the only symmetry which the molecule utilizes in building the crystal. As far as the space group, then, the structure is similar to certain other symmetrically substituted benzene derivatives, and to the naphthalene-anthracene series. With durene, however, the dimensions of the cell give no clue as to the orientation of the molecules, and the further analysis must depend upon the measurement of the intensities of the X-ray reflections.

2. *Experimental—Measurement of Intensities.*

The accurate measurement of the intensities of this compound presents considerable difficulties. Crystals can be obtained in the form of thin plates or prisms, the large face being the (001). Twinning is usual on this face. The crystals are soft, melting at 80°, and very volatile, a small specimen only lasting about half an hour in the open.

It was found that the difficulty of twinning could be overcome by careful crystallization from benzene, when good untwinned specimens were obtained in the form of small prisms. These were cut carefully to the size required (0.4 to 0.1 mg.) with as nearly as possible square sections perpendicular to the zone axis under examination. These small specimens were then sealed off in very thin glass tubes, the uniformity of the glass and its absorption effect on the X-ray beam being tested. Even the thin tubes used were found to stop from 35% to 50% of the copper rays, but, of course, a much smaller fraction of the molybdenum beam.

A complete survey of the relative intensities of the reflections for a number of zones was carried out by the photographic method, employing copper radiation, the procedure being similar to that employed for the anthracene analysis.* Special care had to be taken in estimating the backgrounds owing to extra scattering from the glass tubes. Several short exposures were obtained, however, from a small crystal in the open, by means of one of Dr. Muller's powerful rotating anode X-ray tubes. It was found that these measurements agreed very well with those obtained in the more detailed surveys from the glass protected crystals. As with anthracene, intensities were measured over a range of about 1000 to 1 and special methods were employed to correlate the results over this range.

The general experience is that the smaller crystals lead to higher values for the more powerful reflections. The values obtained for these reflections from

* 'Proc. Roy. Soc.,' A, vol. 140, p. 79 (1933).

the smallest available crystals are taken to be correct, without further correction for extinction, and the values are correlated with the measurements of the weaker reflections from the larger crystals used for the extended surveys. An example of this correlation is given in Table I.

Table I.—Integrated intensity, arbitrary units.

<i>hkl.</i>	Small crystal unprotected. 0.1 mg.	Larger crystal under glass. 0.4 mg.	Combined results.
001	643	505	643
002	280	249	280
003	56	58	57
200	357	338	357
600	16	17	17
20 $\bar{1}$	499	413	499
20 $\bar{3}$	54	53	53
40 $\bar{3}$	—	9	9
601	31	29	30
80 $\bar{3}$	18	18	18

In other experiments it was found that still higher values were obtained for the (001) and (002), so that the true values for the strong reflections remain a little doubtful. But on the whole quite satisfactory correlations were obtained for the reflections within each zone. In further correlating the separate zones there are, of course, fewer common reflections, and the results are correspondingly more uncertain. But again a fairly reasonable agreement was reached in different experiments.

So far only the relative intensity measurements have been described. The absolute values of the structure factors were obtained in the following way. Two of the durene crystals upon which an extended series of relative measurements had been made were selected, and a few reflections from each were carefully measured on the ionization spectrometer. These were compared, under exactly the same tube conditions, with two standard crystals of known reflecting power, *i.e.*, two crystals for which the quantity $E\omega/I$ had been accurately measured.* The absorption of the X-ray beam by the glass tubes surrounding the durene crystals was now carefully measured by exploration with fine pin-hole beams of monochromatic copper and molybdenum rays. The correction for the glass tube, and for the absorption in the crystal itself being ascertained, it was now possible to derive the absolute values for the durene reflections. The two crystals employed gave consistent results with

* For the loan of these two standard reflectors I am greatly indebted to Dr. B. W. Robinson.

copper radiation, but the experiments with molybdenum radiation were somewhat inconclusive. The values used in this paper are taken from the experiments with copper radiation.

The two durene crystals for which absolute measurements were thus obtained were now employed as sub-standards to calibrate all the intensity measurements with absolute values. With the usual formulæ for the "imperfect" crystal, the values of F were now derived, and these are given in Table II (F measured). Owing to the difficulty of handling these crystals, and the large corrections necessary for the glass containers, etc., the final results are perhaps slightly more uncertain than the anthracene measurements. But they are sufficiently accurate to permit a detailed analysis of the crystal structure.

Table II.—Measured and Calculated Values of the Structure Factor.

hkl .	$\sin \theta$ Cu $K\alpha$.	F calculated.	F measured.	hkl .	$\sin \theta$ Cu $K\alpha$.	F calculated.	F measured.
200	0.145	+27	28	20 $\bar{6}$	0.672	-7	2.5
400	0.290	-9.5	9	20 $\bar{5}$	0.550	+2	< 2.5
600	0.435	-10	12.5	20 $\bar{4}$	0.440	-5.5	8
800	0.580	-7	10	20 $\bar{3}$	0.330	-19	18.5
1000	0.725	+2.5	< 3	20 $\bar{2}$	0.224	0	5.5
020	0.267	-13	12.5	20 $\bar{1}$	0.146	+32.5	34
040	0.534	-7	4	201	0.222	+13	12.5
060	0.801	+13.5	9	202	0.325	+5	5.5
001	0.120	+42.5	38.5	203	0.438	-6	5.5
002	0.239	-34.5	37	204	0.551	-8.5	4
003	0.358	-22.5	20	205	0.668	0	< 2.5
004	0.478	+1	4	40 $\bar{6}$	0.657	-1	< 2.5
005	0.597	-1	< 3	40 $\bar{5}$	0.549	-9	4.5
006	0.716	-6.5	< 3	40 $\bar{4}$	0.448	-3	4
				40 $\bar{3}$	0.360	+10	9
011	0.180	+3	2.5	40 $\bar{2}$	0.291	+3	6
012	0.272	-9	10	40 $\bar{1}$	0.266	-14	17
013	0.381	-6.5	6	401	0.357	-2.5	< 2
014	0.495	+4	< 3	402	0.444	-1.5	2.5
015	0.610	+1	< 3	403	0.545	+7	3.5
016	0.725	-6.5	< 3	404	0.650	+11.5	9
021	0.291	-6.5	5	405	0.760	+3.5	2
022	0.357	-0.5	3.5	60 $\bar{6}$	0.672	+9	3.5
023	0.445	-1.5	3	60 $\bar{5}$	0.581	+12.5	3
024	0.545	+4	2	60 $\bar{4}$	0.500	-2	2
025	0.653	+5	4.5	60 $\bar{3}$	0.439	-19.5	12
026	0.761	+1	< 3.5	60 $\bar{2}$	0.403	-8	9
031	0.417	+0.5	3	60 $\bar{1}$	0.402	+8.5	2
032	0.465	+1	< 2.5	601	0.496	-24	18.5
033	0.537	0	< 2.5	602	0.576	-2	< 2.5
034	0.621	-2	< 2.5	603	0.665	+18.5	11.5
035	0.717	-1.5	< 2.5	604	0.765	+12	5.5
041	0.546	-6.5	5	80 $\bar{6}$	0.718	+17	9.5
042	0.583	-4	< 3	80 $\bar{5}$	0.645	+12	6.5
043	0.642	+1	< 3	80 $\bar{4}$	0.585	-9	9
044	0.715	+6	2	80 $\bar{3}$	0.545	-14	14.5
051	0.678	-0.5	< 2.5	80 $\bar{2}$	0.530	-3.5	< 2.5
052	0.710	+1.5	< 3.5	80 $\bar{1}$	0.544	-2.5	< 2.5
				801	0.638	-2	3
				802	0.711	+2.5	2.5

Table II—(continued).

<i>hkl.</i>	$\sin \theta$ Cu K α .	F calculated.	F measured.	<i>hkl.</i>	$\sin \theta$ Cu K α .	F calculated.	F measured.
100 $\bar{5}$	0.731	+ 1	< 2.5	550	0.758	+ 0.5	< 4.5
100 $\bar{4}$	0.690	+ 3.5	< 3	610	0.455	+ 3	4.5
100 $\bar{3}$	0.668	0	2.5	620	0.510	+ 4	3
100 $\bar{2}$	0.665	- 5.5	3	630	0.589	+ 0.5	< 3.5
100 $\bar{1}$	0.686	- 2.5	< 3	710	0.525	- 5	3.5
110	0.152	+29	27	720	0.574	- 0.5	< 3.5
120	0.276	- 6.5	13	810	0.595	- 4	3
130	0.407	+ 3	< 2	910	0.666	- 5.5	2
140	0.539	+ 6	2	11 $\bar{4}$	0.470	- 9	5
150	0.670	+ 2	< 3	11 $\bar{3}$	0.360	- 7	4.5
210	0.196	+49	56.5	11 $\bar{2}$	0.256	- 5	5
220	0.303	+12	14	11 $\bar{1}$	0.174	+20	19
230	0.426	+ 1	< 3	111	0.210	+11.5	10
240	0.553	+ 1.5	< 3.5	112	0.305	- 9.5	9
250	0.682	-11.5	8	113	0.415	- 7.5	7.5
310	0.256	+23	30.5	12 $\bar{1}$	0.290	+ 2	< 3.5
320	0.345	+17.5	14.5	13 $\bar{1}$	0.415	- 5.5	7
330	0.455	- 8	5	21 $\bar{2}$	0.260	-11.5	12.5
340	0.575	- 6	6	22 $\bar{3}$	0.422	- 5	< 5
350	0.700	+ 7	< 5	22 $\bar{2}$	0.347	- 9.5	10.5
410	0.319	+ 8.5	10.5	22 $\bar{1}$	0.304	+ 4.5	< 3
420	0.393	+12	5.5	221	0.347	- 8.5	11
430	0.492	+ 3.5	< 3.5	222	0.421	-17	15
440	0.606	+ 6.5	3.5	23 $\bar{2}$	0.459	+ 3	< 5
450	0.725	- 4	2	31 $\bar{3}$	0.362	+17	15
510	0.386	- 4	< 3	32 $\bar{3}$	0.430	+ 7.5	6
520	0.450	+13	9.5	33 $\bar{3}$	0.523	+ 2.5	< 5
530	0.539	+11	8	33 $\bar{1}$	0.449	- 8.5	5.5
540	0.644	- 6.5	3.5	41 $\bar{4}$	0.468	- 8	5

3. Analysis of the Structure.

Even with the assumption that only the carbon atoms have any appreciable scattering power for X-rays, the durene structure still contains 15 independent parameters. The problem is therefore much too complex to be undertaken without some further guiding principles. The chemical structure states the relative positions of the atoms in the molecule, but the exact form and dimensions of the ring and side groups are unknown. Now, the results of the anthracene investigation have shown that even in a complex structure where the molecule does not coincide with any crystal plane, the aromatic rings are regular plane hexagon structures, to quite a high degree of accuracy. It seems a reasonable assumption, then, to take a plane model of the durene structure, based upon the anthracene dimensions, as shown in fig. 2.

The carbon to carbon distance in the ring is 1.41 A., and the CH₃ groups are placed at the greater distance of about 1.56 A. from the benzene ring, but

a small variation of the latter distance is quite unimportant at the present stage of the analysis.

The problem now reduces to the much simpler one of finding the orientation of this structure in the crystal. The success with which the measured structure factors can be explained by means of this model must be the justification for using it. The finer details of the structure, *e.g.*, the exact position and scattering power of the CH_3 groups, can only be settled by a more detailed Fourier

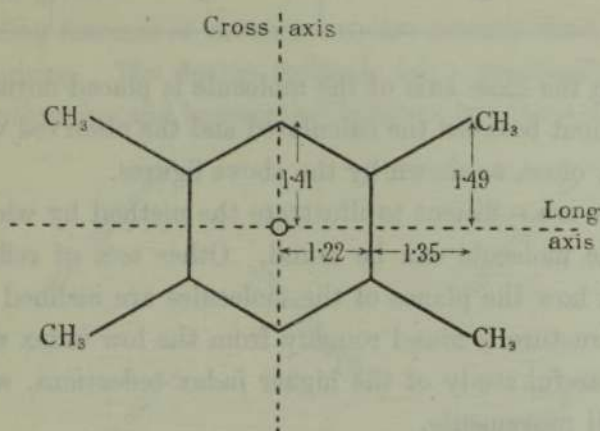


FIG. 2.—Durene model.

analysis. Unfortunately, any such Fourier analysis must be preceded by a careful trial and error analysis, in order to decide the phase constants of each term.

The durene crystal resembles the naphthalene-anthracene type by its tabular or flaky form, the (001) being by far the most important face. It can at once be shown, however, that there is no possibility of the molecules lying in this plane. If they did, the structure factor for the (001) would have a value of about 106* and the higher orders would fall off normally in intensity. The measured value of $F(001)$ is actually only 39, with almost normal decrease to the (003), when the value drops abruptly almost to zero.

Analogy with the naphthalene-anthracene structures, and the pseudo-orthorhombic nature of the lattice (compare fig. 1) suggests the possibility of the long axis of the molecule being nearly normal to the (001) plane. But this possibility can be entirely ruled out by a simple calculation which gives the values shown in Table III for the structure factors for this orientation.

* In these calculations the graphite-anthracene atomic f -curve for carbon is employed. The formulæ for calculating the geometrical structure factors for this space group have already been given ('Proc. Roy. Soc.,' A, vol. 125, p. 542 (1929)).

Table III.

<i>hkl.</i>	F calculated Long axis normal to (001).	F calculated Cross axis normal to (001).	F measured.
001	3	43	39
002	2	38	37
003	2	24	20
004	4	5	4
005	27	2	<3

However, when the cross axis of the molecule is placed normal to the (001) plane, the agreement between the calculated and the observed values for these reflections is very close, as shown by the above figures.

These examples are sufficient to illustrate the method by which the correct orientation of the molecule can be found. Other sets of reflections can be employed to find how the planes of the molecules are inclined to each other. In general the structure is found roughly from the low index reflections, and is refined by a careful study of the higher index reflections, which are more sensitive to small movements.

The best agreements have been obtained for the following orientation. χ , ψ and ω are the angles which the long axis of the molecule makes with the a , b and c' (perpendicular to a and b) crystal axes, χ' , ψ' and ω' are the corresponding angles for the cross axis of the molecule (compare fig. 2). Any three of these quantities can be treated as independent parameters. Then

$$\begin{array}{ll} \chi = 47^\circ & \chi' = 97^\circ \\ \psi = 43^\circ & \psi' = 90^\circ \\ \omega = 85^\circ & \omega' = 7^\circ \end{array}$$

The structure factors calculated for this position are compared with the measured structure factors in Table II.

4. Discussion of Results.

It will be seen that the average agreement between the calculated and observed values is fairly good, and is at least sufficient to determine the sign, or phase constant of all but a few of the weaker reflections beyond any reasonable doubt. Trials of different positions seem to show that while movements of up to 3° have not much effect, yet a movement of 5° in any direction will destroy many of the agreements found. There remains the possibility that some distortion of the model used, *e.g.*, in regard to the position of the CH_3

groups, combined with a movement in some direction, might improve the agreements between the calculated and the observed values. Owing, however, to the good results obtained for all the stronger reflections, it seems clear that such alterations must be of a small order of magnitude. It is hoped to obtain a clearer picture of the fine detail of the structure by means of a double Fourier analysis which is now being undertaken. It is important to emphasize, however, that such a Fourier analysis must depend in its main outlines upon the analysis now given.

The outstanding features of the structure are already clear, and the result is somewhat surprising. The durene molecule has a practically flat or disc-like form as with anthracene and hexamethyl benzene, but these discs are arranged

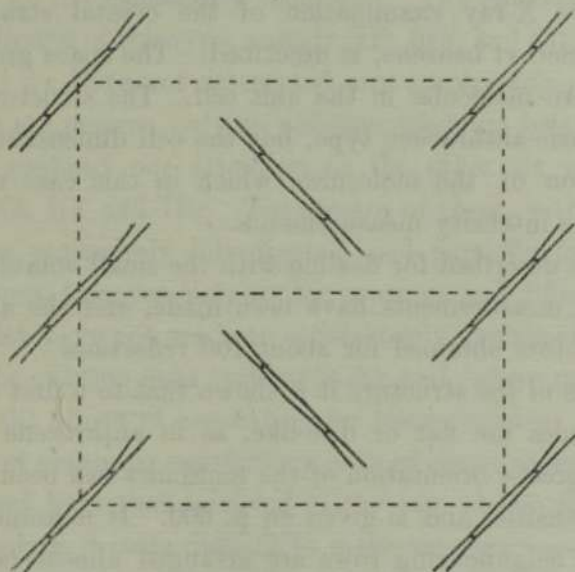


FIG. 3.—Projection on the (001).

almost perpendicularly to each other, instead of being parallel as they are in hexamethyl benzene.* The arrangement is best seen by projecting the structure normally on to the (001) plane, as shown in fig. 3. Owing to the fact that the molecules are tilted only about 7° away from the normal to this plane ($\omega' = 7^\circ$) the skeleton molecules of fig. 2 project almost into straight lines in this diagram.

The closest sideways distance of approach between atoms in adjacent molecules is 3.71 Å., a figure which may be subject to a small variation when the structure is refined. But it is remarkably similar to the corresponding figure for anthracene of 3.77 Å. The gap between the ends of the molecules

* Lonsdale, 'Proc. Roy. Soc.,' A, vol. 123, p. 499 (1929).

along the *c* axis is of the order of 4.2 Å., a figure again very similar to the anthracene result (4.06).

With regard to the other physical properties of the crystal, I am indebted to Mr. J. D. Bernal for an optical examination. His results are consistent with the molecular orientation arrived at in this analysis, the refractive indices showing that there is no possibility of the molecules being parallel.

In conclusion I wish to thank Sir William Bragg, O.M., F.R.S., and the Managers of the Royal Institution for their interest in this work.

5. Summary.

A quantitative X-ray examination of the crystal structure of durene, 1.2.4.5-tetramethyl benzene, is described. The space group is C_{2h}^5 ($P2_1/a$), and there are two molecules in the unit cell. The structure is thus similar to the naphthalene-anthracene type, but the cell dimensions give no clue as to the orientation of the molecules, which in this case must be deduced directly from the intensity measurements.

A technique is described for dealing with the small volatile crystals. Integrated intensity measurements have been made, and the absolute values of the structure factors obtained for about 100 reflections.

In the analysis of the structure it is shown that to a first approximation at least, the molecules are flat or disc-like, as in anthracene and hexamethyl benzene. The precise orientation of the molecules has been obtained from a study of the intensities and is given on p. 600. It is found that the planes of molecules in neighbouring rows are arranged almost perpendicularly to each other, instead of being parallel, as might be expected. The closest distance of approach between atoms in adjacent molecules is about 3.7 Å., very similar to the distance found for anthracene (3.8 Å.).
